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(54) Title: THE USE OF LIGNINS IN THERMOPLASTICS

(57) Abstract: The instant invention is directed to the use of lignin in thermoplastics (such as: ultra-high molecular weight polyeth-
ylene (UHMWPE)). In the first aspect of the invention, lignins are added to a lead acid battery separator comprising a microporous
membrane including an ultra-high molecular weight polyethylene, a filler, and a processing oil. In the second aspect of the invention,
lignins are used as a processing aid in thermoplastics.

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THE USE OF LIGNINS IN THERMOPLASTICS

Related Application

This application is a continuation-in-part of co-pending U.S. application Serial No. 09/677,435 filed October 3, 2000.

Field of the Invention

This invention is directed to the use of lignins in thermoplastics (such as: ultra-high molecular weight polyethylene (UHMWPE)).

Background of the Invention

Lignin is a by-product of wood pulping operations. Lignin's chemical structure is extremely complex. Lignin is generally accepted to be a three dimensional, crosslinked polymer comprised of three different phenyl propenol moieties. The relative amounts of the three monomeric compounds, coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, vary with the sources of the lignin. Grass lignins, such as obtained from rice, corn, or sugar cane, are comprised predominantly of coumaryl and coniferyl alcohols. Softwood lignins, such as obtained from spruce, pine, redwood, cedar, and the like, are made up of predominantly coniferyl alcohol alone. Hardwood lignins are comprised of mostly coniferyl and sinapyl alcohols. Hardwood lignins are

obtained, or substantially obtained, from oak, cherry, maple, birch, sweet gum, mahogany, and the like.

A thermoplastic refers to a polymer that softens or melts when exposed to heat and returns to its original condition when cooled. Ultra-high molecular weight polyethylene (UHMWPE) refers to a polymer with molecular weight greater than 1 million and preferably in the range of about 5 million to about 7 million. UHMWPE has many unique properties, but it is extremely difficult to process, i.e., form into usable shapes. Conventional extrusion and molding techniques can not be used. When extrusion techniques are used, the energy added to the polymer by the extruder may cause chain scissions (e.g., thermal degradation) which, in turn, detrimentally effects the polymer. Rubin, I.I., Editor, *Handbook of Plastic Materials and Technology*, John Wiley & Sons, Inc., NYC, NY, (1990), p. 349-354, Stein, H.L., "Ultra High Molecular Weight Polyethylene (UHMWPE)", *Engineered Materials Handbook, Vol. 2 Engineering Plastics*, ASM International, Metals Park, OH, 1988, and U.S. Patent No. 4,778,601, each is incorporated herein by reference. One method of extruding UHMWPE is to mix the UHMWPE resin with a mineral oil (or plasticizer), for example 80-98% by weight UHMWPE and 2-20% by weight mineral oil. The uniformly dispersed oil allows the UHMWPE to flow more easily through the extruder. See U.S. Patent No. 4,778,601.

In the first aspect of the invention, lignins are added to an ultra-high molecular weight polyethylene battery separator for a lead acid battery for, in part, reducing antimony poisoning.

Poisoning of lead acid storage batteries is known. One poison is antimony (Sb) which is an alloying component of the lead used in the batteries. Antimony poisoning causes a reduction in hydrogen overvoltage. Several solutions to the antimony poisoning problem have been suggested. For example, see: U.S. Patent 5,221,587 - an uncrosslinked natural or synthetic rubber is a layer on or incorporated into microporous or glass fiber separators (also see column 2, line 51 - column 3, line 14 for a discussion of additional solutions); U.S. Patent 5,759,716 - organic polymers having an affinity for the metal impurity (e.g., Sb) are incorporated into, for example, the separator; European Published Application No. EP 0 910 130 A1 - thiolignins are incorporated into fibrous separators; and Japanese Published Application (Kokai) No. 11-191405 - lignins are impregnated or coated on a glass mat separator.

In the second aspect of the invention, lignins are added to thermoplastic polymer formulations to act as a processing flow aid.

Summary of the Invention

The instant invention is directed to the use of lignins in thermoplastics (such as: ultra-high molecular weight polyethylene (UHMWPE)). In the first aspect of the invention, lignins are added to a lead acid battery separator comprising a microporous membrane including an ultra-high molecular weight polyethylene, a filler, and a processing oil. In the second aspect of the invention, lignins are used as a processing aid in thermoplastics.

Detailed Description of the Invention

In the first aspect of this invention, a lignin is added to a microporous battery separator for a lead acid battery made from ultra-high molecular weight polyethylene. The lignin acts as an antimony suppressor which reduces antimony poisoning within the battery. Battery separators made with ultra-high molecular weight polyethylene are known. See for example U.S. Patent 3,351,495; and Besenhard, J.O., Editor, *Handbook of Battery Materials*, Wiley-VCH, NYC, NY (1999) p. 258-263, both are incorporated herein by reference.

The lead acid battery separator generally comprises a microporous membrane made from UHMWPE, fillers, processing oil and lignin. The microporous membrane has an average pore size in the range of about 0.1 to about 1.0 micron, a porosity greater than 10% (preferably between about 55% and about 85%; and most

preferably between about 55% and about 70%), and the pore structure is referred to as an open cell structure or interconnected pore structure. The membrane generally comprises about 15-25% by weight UHMWPE, 50-80% by weight filler, 0-25% by weight process oil, and 5-20% lignin. Additionally, minor amounts of processing aids may be added. Preferably, the membrane comprises 17-23% by weight UHMWPE, 50-60% filler, 10-20% processing oil, and 5-10% lignin. These materials are mixed and extruded in a known fashion. See, for example: U.S. Patent No. 3,351,495; and Besenhard, J.O., Editor, *Handbook of Battery Materials*, Wiley-VCH, NYC, NY (1999) p. 258-263, both are incorporated herein by reference.

UHMWPE refers to polyethylenes with a molecular weight greater than 1 million, preferably greater than 3 million. UHMWPE are commercially available from Ticona LLC, Bayport, TX, and Montell, Inc., Wilmington, DE.

Filler refers to high surface area particles with an affinity for the processing oil. Preferred fillers include precipitated silica, oxide compounds, and mixtures thereof. Such silicas are commercially available from PPG, Pittsburgh, PA and Degussa-Huls AG, Frankfurt, Germany. Also see U.S. Patent Nos. 3,351,495 and 4,861,644, incorporated herein by reference, for additional filler suggestions.

Processing oil (or plasticizer) refers to, for example, mineral oil, olefinic oil, parafinic oil, naphthenic oil, aromatic oil, and mixtures thereof. Processing oil performs two functions; first, it improves the processability of UHMWPE, and second, it is the extractable component, which is used to create the microporous structure of separator. Mineral oil is preferred and is commercially available from Equilon of Houston, TX. Also see U.S. Patent Nos. 3,351,495 and 4,861,644, incorporated herein by reference, for additional processing oil (or plasticizer) suggestions.

Lignin refers to those by-products of wood pulping operations having extremely complex chemical structures that consist primarily of phenyl propane linked together in three dimensions. Lignins include softwood lignins, hardwood lignins, and mixtures thereof. Oak or maple flour may also be used, but because the lignins have not been separated from the cellulose fibers, they are more difficult to process. Hardwood lignins are preferred. Such lignins are commercially available from Westvaco Corp., Charleston, SC under the product name of PC-1369.

Further explanation of this aspect of the invention will be set out in the examples below.

In the second aspect of the instant invention, a lignin may be added to a thermoplastic polymer as a processing aid (e.g., flow lubricant).

In general, it has been found that when up to 10% by weight of the lignin is added to the thermoplastic polymer or the thermoplastic polymer formulation that beneficial results are obtained. Those results include decreased process temperature and polymer viscosity, and increased strength of end product. While not wishing to be bound by the following, it is believed that the lignin is able to reduce thermal degradation (chain scission) of the polymer during processing.

A thermoplastic polymer formulation preferably refers to a mixture of thermoplastic polymer, processing oil (or plasticizer), and lignin. In general, the formulation may be 60-80% thermoplastic polymer, up to 20% processing oil, and up to 10% lignin. Preferably, the formulation may be about 70-80% thermoplastic polymer, 15-20% processing oil, and 5-10% lignin.

A thermoplastic polymer refers to a polymer that softens or melts when exposed to heat and returns to its original condition when cooled. Natural substances that exhibit this behavior are crude rubber and a number of waxes; however, the term is usually applied to synthetics such as polyvinyl chloride, nylons, fluoropolymers, polyethylene (including ultrahigh molecular

weight polyethylene), polystyrene, polypropylene, acrylic resins, other macromolecules, and combinations thereof. Preferably, the thermoplastic polymer is a polyolefin. Most preferably, the thermoplastic polymer is ultrahigh molecular weight polyethylene (UHMWPE). The thermoplastic polymer may also be a mixture of the polymer and a filler. The filler is as discussed above. The ratio of filler to product is about 1.2:1 to about 5:1, preferably about 2.8:1.

Processing oil (or plasticizer) refers to, for example, mineral oil, olefinic oil, parafinic oil, naphthenic oil, aromatic oil, and mixtures thereof. Also see U.S. Patent Nos. 3,351,495 and 4,861,644, incorporated herein by reference, for additional processing oil (or plasticizer) suggestions.

Lignin refers to those by-products of wood pulping operations having extremely complex chemical structures that consist primarily of phenyl propane linked together in three dimensions. Lignins include softwood lignins, hardwood lignins, and mixtures thereof. Hardwood lignins are preferred. Such lignins are commercially available from Westvaco Corp., Charleston, SC under the product name of PC-1369.

Further explanation of this aspect of the invention will be set out in the examples below.

Examples

The formulations set out in Table 1 were prepared.

TABLE 1
(% By Weight)

Sample	Polymer (UHMWPE)	Filler (Silica)	Oil (Mineral Oil)	Minor Ingredients	Lignin
1	22.1	57.9	17.2	2.8	0
2	22.0	57.1	17.1	2.8	1 (Hardwood)
3	20.9	54.3	17.0	2.8	5 (Hardwood)
4	20.3	52.9	17.0	2.8	7 (Hardwood)
5	20.2	52.5	17.0	2.8	7.5 (Hardwood)
6	19.5	50.6	17.0	2.9	10.0 (Hardwood)
7	20.2	52.5	17.0	2.8	7.5 (Softwood)
8	19.5	50.6	17.0	2.9	10.0 (Softwood)
9	16.9	43.3	17.0	2.8	20.0 (Softwood)
10	20.9	54.3	17.0	2.8	5.0 (Oakwood flour)
11	19.5	50.6	17.0	2.9	10.0 (Oakwood flour)
12	20.9	54.3	17.0	2.8	5.0 (Maplewood flour)
13	20.2	52.5	17.0	2.8	7.5 (Maplewood flour)
14	19.5	50.6	17.0	2.9	10.0 (Maplewood flour)
15	16.9	43.3	17.0	2.8	20.0 (Maplewood flour)

The formulations of Table 1 set out in Table 2 were tested for Sb suppression. Results below were obtained via a cyclic voltammetry technique. Cyclic voltammetry techniques are known. Dietz, H., et al, "Influence of substituted benzaldehydes and their derivatives as inhibitors for hydrogen evolution in lead/acid batteries," 53 Journal of Power Sources 359-365 (1995), incorporated herein by reference.

TABLE 2

Sample	Sb Peak Height (mA)	Current (mA) at start of sweep @ -1.100 V
Control (15ppm Sb)	2.8	1.9
3	0.1	0.0
5	0.0	0.1
6	0.1	0.0
7	0.1	0.1
8	0.1	0.1
9	0.1	0.1
10	0.3	0.1
11	0.1	0.0
12	0.0	0.1
13	0.0	0.1
14	0.0	0.1
15	0.0	0.1

The formulations of Table 1 set out in Table 3 were tested for viscosity reduction. Formulations were tested using Kayeness Rheometer Galaxy III Model 9052, available from Kayeness, Inc. of Morgantown, PA.

TABLE 3

Sample	1	2	3	4
Shear rate (1/sec)	Shear Viscosity (Pa-sec)			
1368	1.94E+02	1.76E+02	1.58E+02	1.54E+02
547	4.32E+02	3.93E+02	3.52E+02	3.41E+02
164	1.01E+03	8.97E+02	8.68E+02	8.44E+02
55	2.01E+03	1.96E+03	1.92E+03	1.80E+02
16	4.83E+03	4.51E+03	4.77E+03	4.59E+03
6	1.23E+04	1.18E+04	1.19E+04	1.14E+03
2	2.27E+04	2.21E+04	1.93E+04	2.30E+04
1	9.88E+04	8.57E+04	8.32E+04	9.40E+04

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appended claims, rather than the foregoing specification, indicating the scope of the invention.

In the Claims:

1. A battery separator for lead acid batteries comprising:
a microporous membrane including
an ultra high molecular weight polyethylene,
a filler,
a processing oil, and
a lignin.
2. The separator of claim 1 wherein said lignins being
selected from the group consisting of softwood lignins, hardwood
lignins, and mixtures thereof.
3. The separator of claim 1 wherein lignin comprises about
5-20% by weight of said membrane.
4. The separator of claim 1 wherein said lignin comprises
hardwood lignin.
5. The separator of claim 1 wherein said lignin comprises
about 5-10% by weight of said membrane.
6. A lead acid battery including the separator of claim 1.

7. A battery separator for a lead acid battery comprises:
a microporous membrane having an open cell structure
with pores sizes in the range of about 0.1 to about 1 micron and
porosity greater than 10%, and further comprising
about 15-25% by weight of said separator being an ultra
high molecular weight polyethylene;
about 50-80% by weight of said separator being a
filler;
less than about 25% by weight of the separator being a
processing oil;
about 5-20% by weight of the separator being a lignin.

8. The separator of claim 7 wherein said filler being
selected from the group consisting of precipitated silica, oxide
compounds, and mixtures thereof.

9. The separator of claim 7 wherein said oil being
selected from the group consisting of mineral oil, olefinic oil,
parafinic oil, naphthenic oil, aromatic oil, and mixtures thereof.

10. A thermoplastic polymer formulation comprising:
up to about 80% by weight of the formulation being
thermoplastic polymer;
up to about 20% by weight of the formulation being a
processing oil, and

up to about 10% by weight of the formulation being a lignin.

11. The formulation of claim 10 wherein said lignin being a hardwood lignin.

12. The formulation of claim 10 wherein said polymer being a polyolefin.

13. The formulation of claim 10 wherein said polymer being an ultrahigh molecular weight polyethylene.

14. The formulation of claim 10 wherein said polymer includes a filler.

15. A method for improving the processing of thermoplastic polymer comprising the step of:

adding a lignin to a thermoplastic polymer prior to the processing.

16. The method according to claim 15 wherein up to 10% by weight of said lignin being added.

17. The method according to claim 15 wherein the lignin being added to a blend of polymer and processing oil.

18. The method according to claim 15 wherein the polymer being a polyolefin.

19. The method according to claim 15 wherein the polymer being an ultrahigh molecular weight polyethylene.

20. The method according to claim 15 wherein the lignin being a hardwood lignin.